

8.—Concretionary Sandstones from the Learmonth Formation, Carnarvon Basin, Western Australia

By J. E. Glover*

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Bore cores of impure, fine- to very fine-grained quartz sandstones from the Jurassic Learmonth Formation contain small calcareous and sideritic concretions. Other important constituents of the rocks are widely disseminated siderite crystals, organic remains (shells, wood fragments, spores and probable algal fragments), pyrite and sparse haematite. Pyrite formed rapidly near the sediment-water interface, apparently from bacterial action in more or less enclosed micro-environments of putrefaction, such as wood cells and spores. Many minute spherical to subspherical pyrite grains, after solution in nitric acid, leave a cellular residue that closely resembles individual spores or spore fragments. The concretions formed shortly after the pyrite, before appreciable sedimentary compaction, and preserve delicate organic structures. A little haematite, probably formed elsewhere in oxygenated conditions, has survived. Deposition in a marine basin that may have been silled, and the presence of short-lived and varied micro-environments near the sediment-water interface, are suggested to explain the mineralogy and texture of the concretionary sandstones.

Introduction

The Learmonth Formation is a sequence of interbedded sandstone, conglomerate, siltstone and shale of Middle and Upper Jurassic age in the Carnarvon Basin, Western Australia. The formation is encountered between depths of 3,990 feet and 6,200 feet in West Australian Petroleum's Rough Range No. 1 bore, and is found in other nearby bores. It has been formally defined and briefly described by McWhae, Playford, Lindner, Glenister and Balme (1958). The Learmonth Formation is believed by those authors to be probably a condensed paralic facies equivalent of part of the Dingo Claystone, a sequence mainly of carbonaceous silty claystone and siltstone that was penetrated for 11,463 feet by Cape Range No. 2, without reaching the bottom.

Cores from the Learmonth Formation† in which concretions have been observed are as follows:

Rough Range No. 1—			ft	ft
core 18	4,441-4,444	
core 18	4,444-4,447	
core 18	4,447-4,452	
core 19	4,668-4,677	

The top three specimens are impure, fine- to very fine-grained quartz sandstones containing calcite, shell and plant remains, siderite, pyrite, argillaceous material, black iron ores, haematite and muscovite. The bottom specimen is similar except that calcite and siderite com-

pose 50% of the rock. Siderite is present in most rocks of the Learmonth Formation in Rough Range No. 1. The proportion by weight of organic matter in the rocks has not been determined, but visual estimation suggests that the lowest specimen (from 4,668-4,677 feet) contains the most. Here, about 20% by volume of the concretion is made up of wood fragments, about 5% by shell fragments, and an indeterminate amount by other fine organic matter (probable algal remains, spores, etc.)

Petrography

As the concretionary rocks are similar, only one (core 18, 4,441-4,444 feet) will be described in detail.

Hand Specimen

The rock is dark grey and moderately well consolidated, and contains a light grey, irregularly shaped concretion about 4 cm long (Fig. 1). The most abundant mineral is very fine-grained angular quartz, and other recognizable material includes carbonaceous streaks, muscovite flakes and numerous shell fragments. The fine bedding around the concretion is highly distorted. The rock effervesces in patches with cold dilute HCl, but effervescence is more pronounced in the concretion.

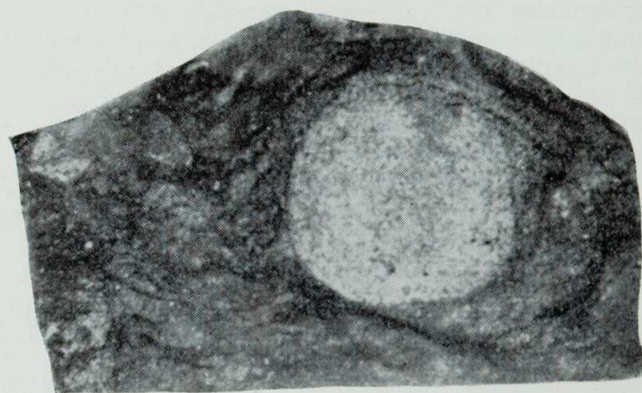


Fig. 1.—Calcareous concretion in very fine-grained, sideritic sandstone from 4441-4444 feet. Note the contorted bedding outside the concretion. Diameter of the concretion, which is about 4 cm long, is 2.5 cm.

Etched Surfaces

Inspection with a binocular microscope of a flat surface that has been etched in cold dilute HCl for several minutes shows that most of the cement in the concretion is calcareous, whereas it is not in surrounding areas. Where calcareous cement is dissolved away, numerous

*Department of Geology, University of Western Australia, Nedlands, Western Australia.

†Made available through the courtesy of West Australian Petroleum Pty. Ltd.

wood fragments with well preserved cell structures remain. Wood in the surrounding rock is almost all distorted and flattened.

Thin Section

Material outside the concretion.—Thin section studies with the petrologic microscope show that about 60% of the rock surrounding the concretion is made up of angular quartz grains, most with a diameter of the order of 0.08 mm. The matrix is made up partly of minute grains of yellow-brown siderite that commonly penetrate borders of adjacent quartz grains, giving them a ragged appearance. The siderite grains are generally rhombs about 0.01 mm in diameter, and their highest refractive index (ω) is close to 1.840. Apart from siderite, the matrix consists mainly of a brown to dark brown clay-sized paste that cannot be resolved under the microscope, although sericite shreds and finely divided organic material can be recognized in places.

Flakes of muscovite are fairly common, and are conspicuous because of their length (up to 1 mm) in the otherwise very fine-grained rock. Many flakes bifurcate and anastomose, being separated by aggregates of minute siderite euhedra (see Fig. 2). It is not clear whether the muscovite is authigenic, and has grown around the siderite, or whether siderite has grown along the (001) cleavage planes, forcing the flakes apart. Optical data for the muscovite are as follows: $\beta = 1.595 \pm .001$, $\gamma = 1.597 \pm .001$, $2V$ (measured on three flakes with the universal stage) = $39^\circ \pm 1^\circ$, $41^\circ \pm 1^\circ$, $44^\circ \pm 1^\circ$. These properties suggest a muscovite containing variable amounts of the picrophengite (Mg rich) molecule, but little of the ferrimuscovite (Fe rich) molecule (Winchell and Winchell 1956, p. 368).

Carbonaceous fragments and streaks are scattered throughout the rock (see Fig. 3), and are generally intimately associated with pyrite. The



Fig. 2.—Thin section (transmitted light) of calcareous and sideritic concretion from 4444-4447 feet. Note splitting of the long mica flake in the centre of the field. Much of the mica outside the concretion has a similar appearance. Diameter of field 1.7 mm.

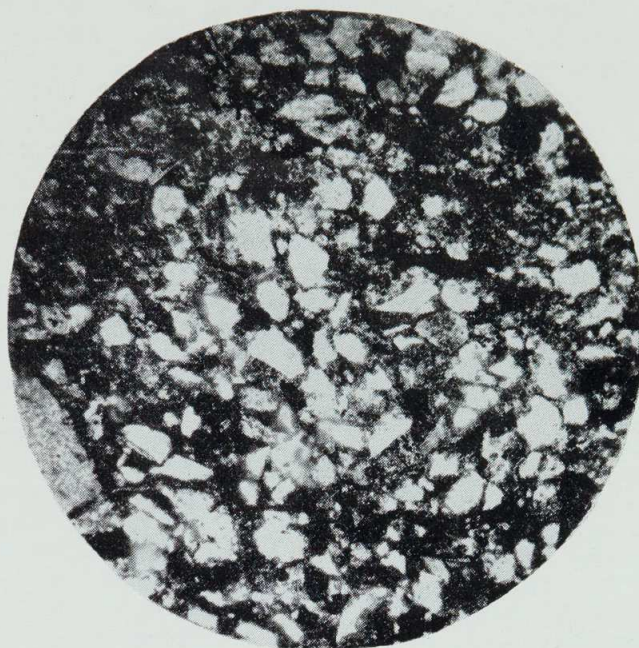


Fig. 3.—Thin section (transmitted light) showing texture outside the concretions in a core specimen from 4659-4668 feet. Note the ragged boundaries of many quartz grains. The grey matrix is mainly very finely divided siderite, and there are also black carbonaceous streaks and black opaque iron minerals. Diameter of field 1.7 mm.

nature of this association is best observed in reflected light, where it can be seen that pyrite grew in the wood cells, and has to some extent preserved the structure of the wood. Where the cells have not been occupied by pyrite however, the wood has been crushed and no trace of them remains. Pyrite is also found as minute spherical bodies (generally from 0.02 to 0.05 mm in diameter) and anhedral grains throughout the rest of the rock. Black opaque grains are ubiquitous, but angular, blood red haematite grains are far less common. A few black opaque grains are partly transformed to haematite, and very rarely, there are composite grains of haematite and pyrite. Other minerals noted include calcareous shell fragments and finely divided calcite, biotite, chlorite, feldspar and leucoxene.

The per cent composition of the rock outside the concretion is visually estimated to be:

Quartz	60
Siderite	12
Calcite (including shell fragments)	8
Woody material	5
Heavy minerals (including pyrite)	5
Muscovite	2
Clay-sized cement, fine organic detritus and other minerals	8

Concretion.—The concretion contains the same minerals as the surrounding rock, but calcite, both as shell fragments and as finely divided cement, is far more abundant. The structure of much of the organic material is far better preserved, however, and will be briefly described.

The structure of the wood has been well preserved (see Figs. 4, 5 and 6). Some of the cells are filled with pyrite, or partly filled by approximately spherical pyrite bodies, but the cell walls have not been replaced. Other cells contain

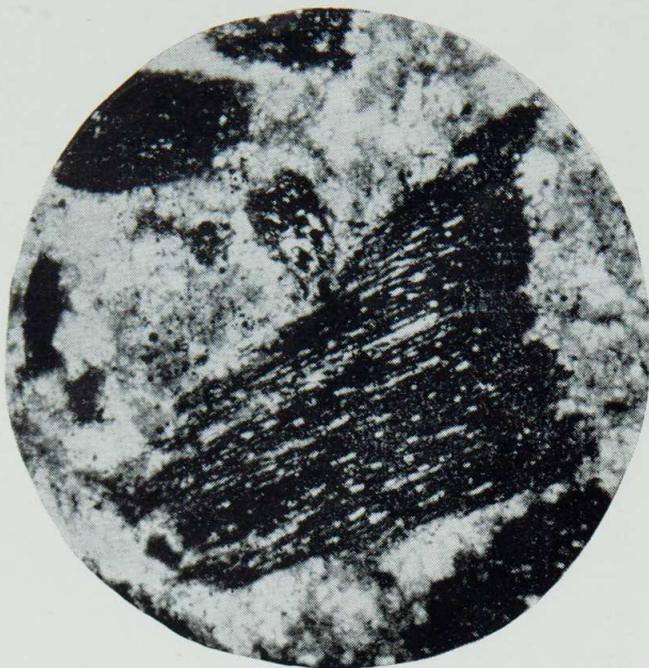


Fig. 4.—Thin section (transmitted light) of wood fragments in calcareous concretion from 4668-4677 feet. Diameter of field 1.9 mm.

minute pyrite crystals, apparently always octahedra, but their small size (usually less than 0.01 mm) precludes certain determination of the form of many of the crystals. Many wood cells contain no pyrite, and their preservation in the concretion contrasts with their destruction outside it.

A few pale brown, faintly anisotropic ovoid bodies with a length of up to 0.2 mm and a width of about 0.1 mm are present. Their origin is not known, for although they superficially resemble coprolitic pellets, almost all of them contain a core of black opaque mineral, or haematite or a composite grain of the two. In fact, it is notable that many of the haematite grains are so enclosed.

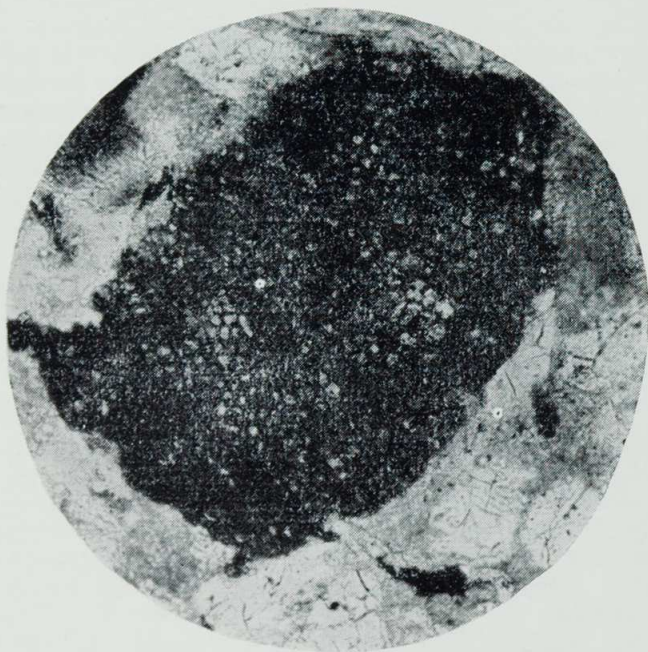


Fig. 5.—Thin section (transmitted light) showing wood fragment in calcareous concretion from 4441-4444 feet. Note preservation of cellular structure. Diameter of field 0.6 mm.

Heavy Minerals

Heavy minerals from the disaggregated rock were concentrated in bromoform. A black, opaque, slightly magnetic, generally angular mineral (apparently ilmenite) is abundant. The range in magnetic susceptibility of the grains suggests, however, that they are not pure ilmenite, but intimate mixtures in varying proportions, of ilmenite and magnetite. Strongly magnetic black opaque grains that include some perfect octahedra (magnetite), and red angular grains (haematite) are less common. Some grains are clearly composite, and are made up of haematite and black opaque mineral. There are also rare composite grains of haematite and pyrite. Zircon and brown tourmaline are fairly common as euhedral grains, but less common as rounded grains.



Fig. 6.—Thin section (reflected light) showing wood fragment in calcareous concretion from 4663-4677 feet. Note the preservation of wood structure and the pyrite (white) filling many of the wood cells. Diameter of field 0.7 mm.

Pyrite is almost as abundant as the black opaque grains, and it occurs in three forms, as small approximately spherical grains, as minute and rare octahedra, and as anhedral grains and aggregates. The spherical grains, which commonly range from 0.02 to 0.05 mm in diameter, although many are smaller, superficially resemble minute berries, and are like the framboidal pyritic bodies described by Love (1958). The octahedra seem perfectly euhedral, but their small size (generally less than 0.01 mm) precludes precise observations. The anhedral pyrite attains lengths of up to 0.15 mm, and rarely far greater: some of the larger grains may be aggregates of the two other forms. Identification of the pyrite was confirmed by Mr. J. G. Kay, of the Department of Geology, University of Western Australia, from an X-ray powder diffraction pattern. It is free of marcasite.

When concentrated nitric acid is allowed to seep between a cover slip and a glass slide on which the spherical or subspherical pyrite grains

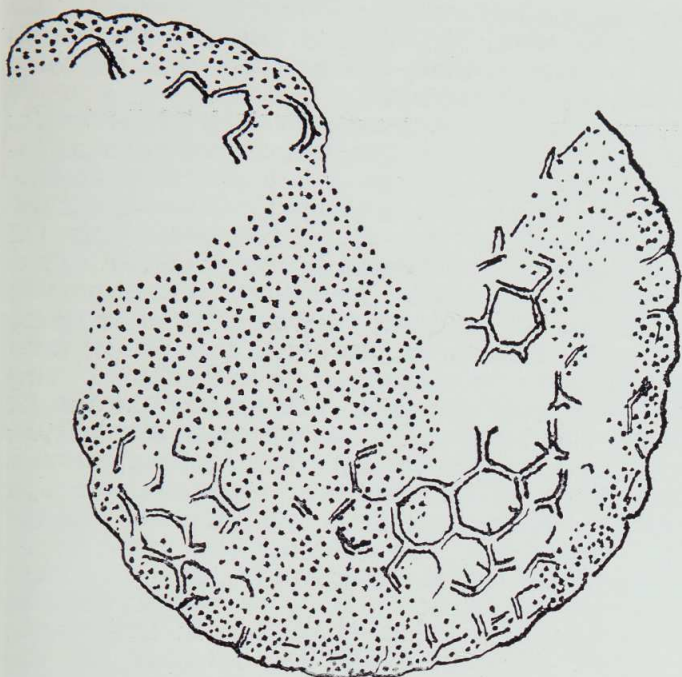


Fig. 7.—Sketch showing residue from a spherical pyrite grain after solution of the pyrite in concentrated nitric acid. The insoluble residual shell has been broken up by the effervescence, and much of it has floated away. Note the polygonal structure, and the grey cloudy material. The diameter of the unbroken shell is about 50μ .

have been placed, a reaction that commonly follows a characteristic sequence can be observed with the binocular and petrologic microscopes. As bubbles from the reaction gather in the liquid, a translucent to cloudy margin appears round the grains. When the margin has reached an eighth to one quarter of the diameter of the grain, it is generally split off by the force of the effervescence. Reaction with the core becomes stronger, and finally all pyrite disappears. Less generally, the hollow shell of translucent to cloudy material is not completely disrupted, and remains more or less intact after complete removal of the pyrite. It appears to be insoluble in the acid, where it has been observed to remain, apparently unaffected, for over one week.

Not all of the translucent material is identical in appearance. Nevertheless, although it is often broken up and obscured by cloudy matter, it can be shown in many grains to consist of a polygonal network. The most common of such networks are composed of six-sided polygons, each cell about 6μ in diameter. Five-sided polygons are also fairly common and four-sided cells have been observed. The cellular material thus appears to form an outer shell in the pyritic spheres, ranging mostly from 0.02 to 0.05 mm in diameter. The thickness of the shells is difficult to determine, and seems generally to be about 5μ . The thin cell walls consist of faintly anisotropic, colourless to pale brown material with a mean refractive index sensibly above that of the surrounding acid ($1.402 \pm .001$), and appear to be somewhat less than 1μ thick. In some grains, although a residue similar in optical properties remains after solution of the pyrite, no regular polygonal

structure can be detected. It is, of course, not unlikely that the structure, whatever its original nature, has been disrupted by the effervescence.

The residue left after solution of the anhedral grains consists of cloudy turbid material and fragments of the anisotropic, colourless to pale yellow material. Fragmentation has been too severe in all such grains treated, to establish the form of the insoluble material, as is possible with many of the spherical and subspherical grains.

Comparison of the insoluble shells remaining after acid treatment of the spherical and subspherical pyrite grains, with organic matter concentrated after treatment of the rock with hydrofluoric acid and centrifuging, reveals some notable similarities. Many of the spores in the organic residue show the same size range as the translucent acid resistant shells derived from the pyrite spheres, and unless flattened, have a similar shape. Moreover, the pattern on the surface of some of the spores can be matched with the polygonal structure of the translucent shells. The correspondence is strong enough to leave little doubt that spores and spore fragments have served as the site of deposition for many of the spherical and subspherical pyrite grains.

The general disruption of the translucent shells caused by effervescence during solution of the pyrite has prevented satisfactory photographs of them from being taken, and the appearance of a typical residue has been sketched (Fig. 7). Toward the end of the experimental work described above, Mr. B. E. Balme (Department of Geology, University of Western Australia) kindly drew the author's attention to a trilete spore in his collection from the Upper Devonian of Libya (Fig. 8). The spore is partly destroyed, and the pattern on the surface resembles that on much of the material extracted from the pyrite grains, and probably owes its origin to the same cause.

Discussion

Deposition of the Learmonth Formation was generally marine, and may have taken place in a silled basin, for the preservation of organic matter is characteristic of environments of restricted circulation. In this respect however,

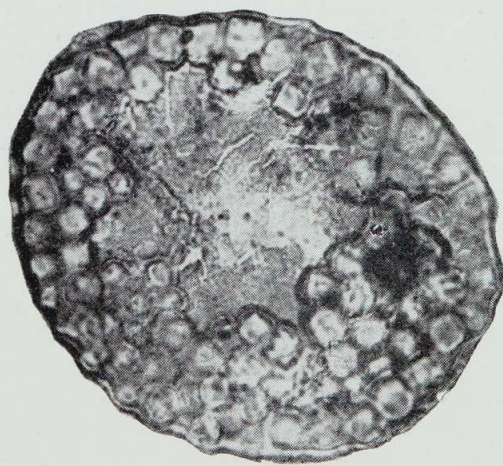


Fig. 8.—Partly destroyed trilete spore from Upper Devonian of Libya. Note similarity of surface pattern to that shown in Fig. 7. Diameter of spore about 80μ .

it is worth noting the view of Krumbein and Garrels (1952, p. 23) that with sufficiently rapid sedimentation, organic matter may accumulate in an open sea neritic environment in mildly oxidizing waters. This is not incompatible with anaerobic or reducing conditions below the sediment-water interface. The Dingo Claystone, probably in part a deep water facies equivalent to the west, also contains fairly abundant, finely divided carbonaceous matter.

Broadly speaking, preservation of organic matter and formation of pyrite and siderite require anaerobic or reducing conditions. Haematite, on the other hand, forms in an oxidizing environment. There is also a sensitive pH control. Edwards and Baker (1951) show evidence for neutral to mildly alkaline conditions of formation for pyrite, and Krumbein and Garrels (1952, Fig. 8) suggest that pyrite and siderite generally form in alkaline conditions up to a pH of 7.8, whereas calcite normally requires slightly higher alkalinity (7.8+). The factors leading to formation and preservation of the above minerals in a marine environment are very likely, however, to be far more complex than those just indicated. Evidence from the Learmonth rocks suggests that short-lived and variable micro-environments played a large part in establishment of their ultimate mineralogy and texture. Some of these micro-environments will now be considered.

Pyrite

The intimate association of much of the pyrite with wood fragments has been noted. There is no evidence in these rocks that pyrite replaces wood, as it has been stated to do elsewhere by other authors. In the concretions, where the wood has not been squashed, pyrite completely fills some of the wood cells and in others forms minute spherical and subspherical grains, and even smaller crystals (apparently always octahedra). Outside the concretions, the cellular framework has disappeared from flattening, except where sufficient cells were filled with pyrite to preserve evidence of the original texture. Some such wood fragments seem in reflected light to have undergone very little compaction, for almost all the cells were so occupied, and preliminary examination might well give the incorrect impression that pyrite had replaced some of the wood. It is clear, however, that the pyrite formed before significant compaction of the wood, and other evidence given later accords with this view. Minute spherical and subspherical grains of pyrite are also scattered throughout the rock, outside the wood fragments.

The octahedron is the only crystalline form recognized here, and has been the dominant form in authigenic pyrite observed elsewhere by the author. It also figures prominently in descriptions of authigenic pyrite in the literature, although no special significance appears to have been attached to the fact. The findings of Kasizyn (1956) (as summarized in German by Mirtsching*) may, therefore, be of interest. Kasizyn noted that in pyrite from old metamorphic rocks examined by him, the forms de-

veloped include cubes, pentagonal dodecahedra and octahedra. Octahedral pyrite is anomalous and contains cobalt impurities which are held responsible for its habit.

The spherical and subspherical pyrite bodies in the Learmonth Formation resemble those noted in thin section by Brelie and Teichmüller (1953) and Balme (1956), and those separated from the Lower Carboniferous Oil Shale Group of Scotland by Love (1958). Love subjected his pyrite granules to nitric acid treatment with results very like those recorded here. He isolated microfossils from them, and named two new genera, *Pyritosphaera* and *Pyritella*, although their affinities could not be closely defined. He suggested that these organisms generated hydrogen sulphide as a by-product of the anaerobic decomposition of sulphur compounds, and that the gas reacted with iron from the surrounding medium, so precipitating iron sulphide on the organism. Although his genus *Pyritella* resembles some of the polygonal material described in this paper, a rather different origin is indicated for the latter. Organic matter that almost certainly included individual spores and spore fragments was the most likely nucleus for precipitation of many of the spherical pyritic grains of the Learmonth Formation. Precipitation took place before the spores were much compressed.

In summary then, the growth of pyrite occurred very early in the diagenetic history of the rock, probably on or just below the sediment-water interface. Its formation is best accounted for by the action of anaerobic bacteria in more or less enclosed spaces (spores and wood cells) where putrefaction was proceeding. The probable sequence of events has been set forth by Balme (1956). The bacteria reduce sulphate to sulphide at the expense of various organic compounds, and the hydrogen sulphide so formed reacts with ferrous hydroxide to give troilite (FeS). Subsequently, the troilite changes either to marcasite, in slightly acid conditions, or pyrite, in neutral to alkaline conditions.

Siderite and Calcite

Siderite is found almost throughout the Learmonth Formation in Rough Range No. 1, and its usual habit (minute euhedral crystals that penetrate adjacent quartz grains) indicates its authigenic origin. The siderite has changed from greyish to brownish in the laboratory, showing its susceptibility to oxidation, a property noted also by Pettijohn (1957, p. 145). Its formation in sediments, according to Krumbein and Garrels (1952, Fig. 8) is indicative of less strongly reducing conditions than those required for pyrite. In one concretion of which siderite forms most of the cement (from core 18, 4,444-4,447 feet) the wood fragments are perhaps not as well preserved from crushing as in the more calcitic concretions, but they are better preserved than in the surrounding rock.

It seems therefore that siderite and calcite (excluding calcite of shells) formed at about the same time. A sufficiently dense accumulation of either mineral resulted in a concretion: these concretions grew before appreciable compaction of the sediment, but after formation of the pyrite, which they enclose. The comparatively

*Mirtsching, A. (1959).—*Zbl. Miner.* 1957, (1): 109.

early growth of some types of concretion, which preserve contained organic matter from decomposition and crushing, has been known for some time, and there are interesting descriptions of the preservation of fishes (Weeks 1957) and plants (Brelie and Teichmüller 1953) by this means. The rather special conditions leading to formation of concretions are not, however, so easily explained. Weeks suggests that in some stagnant environments where the pH is normally too low for precipitation of calcium carbonate, alkalinity sufficient for deposition may be brought about locally by ammonia evolving rapidly from decomposition of proteinaceous (nitrogen bearing) organic matter. The abundance of shell fragments in the concretions of the Learmonth Formation may be significant but the processes leading mainly to precipitation of siderite instead of calcite in one concretion are not understood. Presumably they result from localized and critical combinations of Eh and pH.

Haematite

The presence of haematite, which is scattered sparsely through the concretions and surrounding rock as discrete grains, and combined with black iron ore, seems anomalous. Organic material, pyrite and siderite compose a mineral suite that accords with the interpretation of an anaerobic or reducing environment, whereas haematite is the product of a well aerated environment. It forms from iron silicates, magnetite, and probably from ilmenite as it develops rapidly in air at high temperatures from that mineral (Karkhanavala and Momin 1959). The presence of many grains of haematite and compound grains including haematite in ovoid pellets, perhaps of coprolitic origin, cannot be explained, but may be due to selection by some organism. A tentative explanation for the presence of haematite is that it formed earlier in a strongly oxidizing environment, perhaps for example, from jaspilites on the Precambrian Shield. It was swept into the basin of deposition with other clastics, and some of it survived the short-lived reducing environment to which it was then subjected.

Conclusions

Evidence from the composition and texture of the concretionary rocks from the Learmonth Formation in Rough Range No. 1 suggests de-

position in an oxygen deficient marine environment, near enough to the coast to receive a fair amount of plant material. The basin may have been silled during deposition of these rocks. Pyrite formed quickly close to the sediment-water interface, especially in micro-environments of putrefaction, such as cells of wood fragments and interiors of spores. Siderite then grew rapidly in an environment assumed to have been generally oxygen deficient and slightly alkaline. Slight variation from these general conditions resulted locally in precipitation of calcite. Concretions, either composed mainly of siderite or calcite, grew before appreciable compaction, preserving contained organic structures. Sedimentary material around the rigid concretions was compacted by superposed sedimentary beds which eventually attained a thickness of many thousands of feet.

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